

FORM PTQ-1390 (Modified)
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

UDS

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/529289

INTERNATIONAL APPLICATION NO.
PCT/IL98/00491INTERNATIONAL FILING DATE
October 8, 1998PRIORITY DATE CLAIMED
October 12, 1997

TITLE OF INVENTION

COATING SYSTEM FOR SUBSTRATES

APPLICANT(S) FOR DO/EO/US

Yaacov ALMOG; Sergio BRANDRISS

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

1. Amendments to the International Application under PCT Article 34 are transmitted herewith as annexes to the IPER
2. Form PTO-1449 listing the art cited in the International Search Report

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/529289	INTERNATIONAL APPLICATION NO. PCT/IL98/00491	ATTORNEY'S DOCKET NUMBER UDS
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20. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

☒ Search Report has been prepared by the EPO or JPO **\$840.00**
~~\$930.00~~

☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) **\$720.00**

☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) **\$790.00**

☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO **\$1,070.00**

☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) **\$98.00**

CALCULATIONS PTO USE ONLY	

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$840.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). ☐ 20 ☐ 30

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	129 - 20 =	109	x \$18.00
Independent claims	6 - 3 =	3	x \$78.00

\$1,962.00
\$234.00

Multiple Dependent Claims (check if applicable). ☒

\$260.00

TOTAL OF ABOVE CALCULATIONS =

\$3,296.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐

\$0.00

SUBTOTAL =

\$3,296.00

Processing fee of **\$130.00** for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). ☐ 20 ☐ 30

\$0.00

TOTAL NATIONAL FEE =

\$3,296.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐

\$0.00

TOTAL FEES ENCLOSED =

\$3,296.00

	Amount to be: refunded	\$
	charged	\$

- ☐ A check in the amount of _____ to cover the above fees is enclosed.
- ☒ Please charge my Deposit Account No. **03-3419** in the amount of **\$3,296.00** to cover the above fees.
A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **03-3419** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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Paul Fenster
SIGNATURE

Paul FENSTER
NAME

33,877
REGISTRATION NUMBER

April 5, 2000
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Y. ALMOG, et al.
Serial Number: Not Yet Assigned
Filed: October 8, 1998 as PCT/IL98/00491
For: COATING SYSTEM FOR SUBSTRATES
Art Unit: Not Yet Assigned
Examiner: Not Yet Assigned

Honorable Commissioner of Patents and Trademarks
Washington DC 20231

PRELIMINARY AMENDMENT

Sir:

Further to the concurrent filing of the U.S. national stage of PCT/IL98/00491, kindly amend the application as follows prior to examination:

IN THE DISCLOSURE

Kindly add, on page 1, after the title:

--RELATED APPLICATION

The present application is a US national stage application of PCT/IL98/00491, filed 8 October 1998.--

IN THE CLAIMS

The following amendments are based on the claims attached to the IPER submitted together with the application.

Claim 3, line 1, delete "or claim 2".

Claim 7, line 1, change "the preceding claims" to --claims 1, 4 or 6--.

Claim 8, line 1, change "1-6" to --1, 4, or 6--

Claim 9, line 1, change "1-6" to --1, 4, or 6--

Claim 10, line 1, change "1-6" to --1, 4, or 6--

Claim 11, line 1, change "1-6" to --1, 4, or 6--

Claim 12, line 1, change "the preceding claims" to --claims 1, 4 or 6--

Claim 14, line 1, change "1-11 or 13" to --1, 4, 6 or 13--

Claim 17, line 1, change "any of claims 14-15" to --claim 14--

Claim 18, line 1, change "any of claims 14-15" --to claim 14--.

Claim 19, line 1, change "1-11 or 13" to --1, 4, 6 or 13--

Claim 20, line 1, change "the preceding claims" to --claims 1, 4, 6 or 13--.

Claim 21, line 1, change "1-19" to --1, 4, 6 or 13--.

Claim 22, line 1, change "1-19" to --1, 4, 6 or 13--.

- Claim 23, line 1, change "the preceding claims" to --claims 1, 4, 6 or 13--.
- Claim 24, line 1, change "the preceding claims" to --claims 1, 4, 6 or 13--.
- Claim 25, line 1, change "the preceding claims" to --claims 1, 4, 6 or 13--.
- Claim 26, line 1, change "the preceding claims" to --claims 1, 4, 6 or 13--.
- Claim 28, line 1, change "the preceding claims" to --claims 1, 4, 6 or 13--.
- Claim 29, line 1, change "the preceding claims" to --claims 1, 4, 6 or 13--.
- Claim 31, line 2, change "1-29" to --1, 4, 6 or 13--.
- Claim 32, line 1, delete "or claim 31".
- Claim 37, line 2, change "1-29 or 32-36" to --1, 4, 6, 13 or 33--; line 3, delete "or claim 31".
- Claim 39, line 1, delete "or claim 38".
- Claim 40, line 1, delete "or 38".
- Claim 41, line 1, change "any of claims 37-40" to --claim 37--.

REMARKS

The present application is a US national application of PCT/IL98/00491. Applicants respectfully request that the claims attached to the enclosed IPER be used as the basis for the present amendments.

The present application, after amendment, contains claims 1-41. The IPER claims have been amended to place them in proper form for examination in the US.

The Examiner is respectfully requested to further review and cite the prior art cited in the PCT application. The art is available to the Examiner in the parent PCT file. To facilitate the citing of the prior art, applicants submit a filled out form 1449 listing the art cited in the PCT search report.

An examination on the merits is respectfully awaited.

Respectfully submitted,
Y. ALMOG, et al.



Paul Fenster
Reg. No. 33,877

April 5, 2000
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COATING SYSTEM FOR SUBSTRATES

FIELD OF THE INVENTION

The present invention is related to the field of printing and in particular to a method of coating substrates to improve adhesion of toner images thereto.

BACKGROUND OF THE INVENTION

Problems of transfer and adhesion of toner images and in particular of liquid toner images, to substrates, is well known. Transfer of images may be effected by electrostatic transfer of toner particles to the substrate, either from an imaging surface such as a photoreceptor or from an image transfer member. Alternatively, image transfer may be effected by heat and pressure, generally from an intermediate transfer member to which the image is first transferred from the imaging surface. Image transfer from an intermediate transfer member, on which the image is generally in a molten state, is often problematic. Usually, some treatment of the substrate surface is required in order to enable good transfer and fixing.

Transfer and adhesion of toner is improved by chemical compatibility of the toner and the substrate for example, chemical bonding by acid-base interaction or chemical similarity leading to mutual bonding.

A common solution to transfer and adhesion problems is the coating of a substrate with an adhesion enhancer, which has an affinity for both the toner material and the substrate. For example, the adhesion of the above mentioned toner types to PET and BOPP can be greatly enhanced by coating the substrates with a layer of Macromelt 6239 (Henkel) which is an amine terminated polyamide. This material adheres well to the substrate and has a high affinity for the toner particle polymer as well. However, it has been found that the shelf life of such coated substrates is limited and the quality of the transfer of toner from an intermediate transfer member to the substrate degrades with time. This aging process of the coating does not seem to effect the adhesion of images which are already transferred to the substrate.

However, as is well known in the art, such substrate processing does not always lead to satisfactory results, especially in digital electrostatic printing.

EP Patent Publication EP 0 789 281, the disclosure of which is incorporated herein by reference, describes a coating system for polypropylene in which the polypropylene is coated with polyethylene and then with ethylene-acrylic acid and minor amounts of filler such as talc or silica and wax and/or pigment.

EP Patent Publication EP 048 481 describes a coating system for coating a polymeric substrate with a first lacquer layer, preferably containing a particulate material. The lacquer layer is overcoated with a toner receptive layer containing a copolymer comprising styrene and/or a styrene derivative and at least one ethylenically unsaturated co-monomer copolymerisable therewith, the copolymer containing at least one free functional acid group. The toner preferably comprises an additional acrylic and/or metacrylic polymer to improve the ink receptivity of the layer. Optionally, an adhesion promoting layer may be situated between the lacquer layer and the polymeric substrate.

US Patent 5,126,198 describes a coated substrate that is not described as being suitable for forming toner images thereon. Rather this material is used as a heat laminatable multi-layer film. The outer, heat laminatable layer comprises a mixture of polymers.

SUMMARY OF THE INVENTION

One aspect of some preferred embodiments of the present invention is a novel approach to the improvement of transferability and/or adhesion of images to substrates, especially plastic substrates.

In a broad view of some preferred embodiments of the invention, a double coating is employed, with an underlayer having a high affinity for the substrate and an overlayer having a high affinity for the toner material. The two layers have a high affinity for each other.

In an exemplary embodiment of this aspect of the invention, the underlayer is a layer of an amine terminated polyamide such as Macromelt 6239 (Henkel) which was mentioned in the background of the invention. The upper layer is formed of material which has a high affinity for toner particles and which is also adheres well to the underlayer. As indicated above, an amine terminated polyamide has a high affinity for a wide range of materials so that this seldom is a problem. Furthermore, the above mentioned deterioration of the properties of the amine terminated polyamide with time does not exist when it is coated with the overlayer.

Exemplary materials which are useful as overlayers include ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer. Preferably, the overlayer consists substantially only of these materials and more preferably consists substantially only of one of these materials. It is noted that these materials adhere rather poorly to untreated PET, BOPP, polycarbonate, polyethylene and vinyl. For some applications it is useful to reduce the degree of acidity of the ethylene acrylic acid copolymer, preferably by Saponification to a level of preferably between 8 and 18% acrylic acid comonomer weight percent, more preferably between 10 and 16%. Unmodified material typically has a acrylic acid comonomer

weight percent of 20%. In preferred embodiments of the invention, the overlayers are free of silica, talk or other such fillers and free of wax or pigments.

A second aspect of some preferred embodiments of the invention relates to substrates which are coated with ethylene acrylic acid copolymer, polyvinyl pyridine or styrene butadiene copolymer, and especially to substrates coated with ethylene acrylic acid copolymer with reduced acidity. Such coated substrates may, in some preferred embodiments of the invention, be plastic substrates such as PET or BOPP or, in other embodiments of the invention, may be paper. Preferably, the overlayer consists substantially only of these materials and more preferably consists substantially only of one of these materials.

A third aspect of some preferred embodiments of the invention relates to the printing of images, preferably toner images and more preferably liquid toner images, on substrates of the invention or which are produced in accordance with the invention. This printing is preferably by transfer of the toner images to the substrate from an intermediate transfer member, to which it was transferred from an imaging surface. Preferred toners are based on one or more of ethylene vinyl acetate (EVA) copolymers, copolymers of ethylene and α , β - ethyleneically unsaturated acid selected from the group consisting of acrylic and methacrylic acids and ionomers such as are produced under the trade name of Surlyn, by Dupont.

There is therefore provided in accordance with a preferred embodiment of the invention, a substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed.

There is further provided, in accordance with a preferred embodiment of the invention a substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

Preferably, the first polymer material comprises a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.

Preferably, the sheet of plastic is PET. Alternatively, the sheet of plastic is BOPP.
5 Alternatively, the sheet of plastic is polyethylene. Alternatively, the sheet of plastic is vinyl. Alternatively, the sheet of plastic is polycarbonate.

In a preferred embodiment of the invention, the overlayer comprises ethylene acrylic acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%. Alternatively, the ethylene acrylic acid
10 copolymer has an acrylic acid comonomer percentage weight of less than 16%.

Alternatively or additionally, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%. Alternatively, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.

In a preferred embodiment of the invention, the overlayer comprises polyvinyl
15 pyridine. Alternatively, the overlayer comprises styrene butadiene copolymer.

In a preferred embodiment of the invention, the underlayer comprises amine terminated polyamide. Alternatively, the underlayer comprises a silane coupling agent. Alternatively, the underlayer comprises amino propyl triethoxy silane.

In a preferred embodiment of the invention, the underlayer has a weight of between 0.1
20 and 1 grams per square meter. Alternatively or additionally, the underlayer has a weight of between about 0.3 and 0.5 grams per square meter.

In a preferred embodiment of the invention, the overlayer has a weight of between 0.1 and 10 grams per square meter. Alternatively or additionally, the overlayer has a weight of between 0.2 and 2 grams per square meter. Preferably, the overlayer has a weight of between
25 about 0.25 and about 0.35 grams per square meter.

Preferably, the overlayer is substantially wax and pigment free.

Preferably, the overlayer is substantially free of particulate matter. Preferably, the underlayer is substantially free of particulate matter. More preferably, both the overlayer and the underlayer are free of particulate matter.

30 Preferably, the substrate comprises only two coating layers.

There is further provided in accordance with a preferred embodiment of the invention, a method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer, the underlayer comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

5 directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed.

There is further provided, in accordance with a preferred embodiment of the invention, a method of producing a coated substrate which a toner image can be adhered comprising:

10 coating a sheet of plastic with a first polymer material as an underlayer;
directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

15 Preferably, the first polymer material comprises a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane.

20 There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet chosen from the group consisting of PET, BOPP, polycarbonate, polyethylene and vinyl and an outer coating consisting substantially only of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

25 Preferably, the sheet is a PET sheet. Alternatively, the sheet is a BOPP sheet. Alternatively, the sheet is a polycarbonate sheet. Alternatively, the sheet is a polyethylene sheet. Alternatively, the sheet is a vinyl sheet.

Preferably, the coating comprises polyvinyl pyridine. Alternatively, the coating comprises styrene butadiene copolymer. Alternatively, the coating comprises ethylene acrylic acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

30 There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet and a coating of ethylene acrylic acid copolymer having an acrylic acid comonomer percentage weight of less than 18%.

Preferably, an ethylene acrylic acid copolymer, as described above, has an acrylic acid comonomer percentage weight of less than 16%. Alternatively, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.

Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer
5 percentage weight of more than 12%.

Preferably, the coating, as described above, has a weight of between 0.1 and 0.4 grams per square meter. Preferably, the coating has a weight of between about 0.25 and about 0.35 grams per square meter.

There is also provided in accordance with a preferred embodiment of the invention, a
10 printing method comprising:

providing a substrate, as described above; and

printing a toner image on the substrate.

Preferably, the toner image is a liquid toner image. Alternatively or additionally, printing comprises transferring the toner image to the substrate using heat and pressure.
15 Alternatively, printing comprises electrostatically transferring the toner image to the substrate.

In a preferred embodiment of the invention, the printing method comprises:

forming the image on an image forming surface;

transferring the image from the image forming surface to an intermediate transfer member; and

20 transferring the image from the intermediate transfer member to the substrate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A substrate according to a preferred embodiment of the present invention, on which a toner image is to be printed, comprises a plastic or other sheet coated with an underlayer having a high affinity for the substrate and an overlayer having a high affinity for the toner
25 material. The two layers have a high affinity for each other.

One preferred, but non-limiting, method for producing such a substrate uses an underlayer of amine terminated polyamide and an overlayer of ethylene acrylic acid copolymer.

The underlayer

To 950 grams of 1-Propanal add 50 grams of Macromelt 6239 (Henkel), amine terminated polyamide, while stirring the mixture. Heat the material to between 40°C and 50°C until a homogeneous and clear 5% solids solution is obtained.

5 This material is applied to a substrate (for example an optionally corona treated BOPP substrate) by coating the substrate with the 5% solids solution and allowing the solution to dry, leaving a coating of preferably between about 0.1 and 0.3 grams of solid per square meter. This coating should be uniform. The coating may be applied by any one of the available methods of coating and, for example, using a rotogravure coating system. Alternatively a
10 flexographic printing system can be used to apply the coating with the settings of the printer controlling the thickness of the coating. However any other suitable coating process (double blade direct applicator, etc.) can be used. Other solution concentrations and other variations on the above described method can also be used.

While thinner and thicker coatings could be used, thinner coatings are not always
15 effective and thicker coatings are more difficult to apply and expensive.

After application of the solution the coating is dried, preferably by an integral heater in the coating apparatus.

The overlayer

To 465 gm of deionized water add 200 g of isopropyl alcohol. This reaction is
20 exothermic. After the mixture cools, add it to 335 g of a dispersion of MP 4990 (32-35%) as supplied by Michelman.

The dispersion is coated onto the underlayer by any convenient coating process, as for the underlayer, to give a coating of between approximately 0.3 - 0.5 grams per square meter although thinner coatings can be used.. If a double coating apparatus is available, the overlayer
25 may be applied immediately over a dried underlayer.

After application of the overlayer solution the coating is dried, preferably by using the dryer integral in the coater. Other drying methods can also be used.

While the above formulation of overlayer material is suitable for printing on web fed material, it will adhere to surfaces with which it comes into contact, while hot, after printings,
30 as, for example, an exit roller. To reduce the hot adhesivity, the degree of acidity of the ethylene acrylic acid copolymer, is reduced, preferably by Saponification to a level of preferably between 8 and 18% acrylic acid comonomer weight percent, more preferably between 10 and 16%. Unmodified material typically has a acrylic acid comonomer weight

percent of 20%. This modified material can be used to directly coat paper and plastic substrates which do not require the adhesion promotion properties of the underlayer.

Other underlayer materials, for example, a silane coupling agent such as amino propyl triethoxy silane, may be used. The primary requirement for an underlayer is that it have high
5 adhesion to the substrate and to the overlayer.

Other suitable overlayer materials include Polyvinyl pyridine (Molecular weight 40,000 to 200,000) (Scientific Polymer Products). Additionally Styronal PK 8717 (BASF) (styrene butadiene copolymer) can be used as the overlayer. These material are preferably coated at a weight of approximately 0.5 grams per square meter.

10 Various bonding mechanisms can be utilized in various embodiments of the present invention. In the above example, the underlayer and overlayer are base and acid respectively. The toner described below is also acidic; however, the toner forms a strong chemical bond with the overlayer. Other materials, in accordance with preferred embodiment of the invention, utilize other types of bonding.

15 In general, a coating thickness (after drying) of between 0.1 to 10 micrometers is preferred. More preferably, the thickness is between 0.2 to 2 microns.

The coated substrates of the present invention are useful with a wide range of toner material which do not transfer easily to and/or adhere well to PET and BOPP. Preferred toners are based on one or more of ethylene vinyl acetate (EVA) copolymers, copolymers of ethylene
20 and α , β - ethyleneically unsaturated acid selected from the group consisting of acrylic and methacrylic acids and ionomers such as are produced under the trade name of Surlyn, by Dupont.

One preferred method of forming a toner is the following:

1) Solubilization

25 1400 grams of Nucrel 925 (ethylene copolymer by Dupont) and 1400 grams of Isopar L (Exxon) are thoroughly mixed in an oil heated Ross double planetary mixer at at least 24 RPM for 1.5 hours, with the oil temperature at 130°C. 1200 grams of preheated Isopar L is added and mixing is continued for an additional hour. The mixture is cooled to 45°C, while stirring is continued, over a period of several hours, to form a viscous material.

2) Milling and Grinding

762 grams of the result of the solubilizing step are ground in a 1S attritor (Union Process Inc. Acron, Ohio), charged with 3/16" carbon steel balls, at 250 RPM, together with 66.7 grams of Mogul L carbon black (Cabot), 6.7 grams of BT583D (blue pigment produced by Cookson), 5 grams of aluminum tri stearate and an additional 1459.6 grams of Isopar L, for eight hours at 30°C.

3) Continuation of Grinding

34.5 grams of ACumist A-12 is added and grinding is continued for an additional 4-12 hours. The resulting particles are fibrous particles having a measured diameter in the range of 1-3 micrometers.

The resulting material is diluted with additional Isopar L and Marcol 82 to give a working developer in which the dry solids portion is about 1.7% and in which the overall ratio of Isopar L to Marcol is between about 50:1 and 500:1, normally about 100:1.

Charge director as described in US patent application 07/915,291 (utilizing Lecithin BBP and ICIG3300B) and in WO 94/02887, in an amount equal to 40 mg/gm of solids, is added to charge the tone particles. Other charge directors and additional additives, as known in the art may also be used.

In a preferred embodiment of the invention the substrate is printed using an intermediate transfer member to transfer images to the substrate and to fuse and fix them thereto. Preferred apparatus for such printing are the E-Print 1000 and the E-Print Omnius printers marketed by Indigo NV.

The present invention has been described utilizing preferred embodiments thereof. It should be understood that the details of the coating processes and exact formulations of the coatings and liquid toners are meant to be exemplary in nature and not to limit the claims. In particular the invention also includes materials which are listed in the summary and claims for the substrate, the underlayer, the overlayer and the toner, as well as different combinations of materials chosen from the four groups of materials. When used in the claims, the words "comprise," "include" and "have" and their conjugations mean "including, but not necessarily limited to."

CLAIMS

1. A substrate suitable for printing a toner image thereon, comprising:
a sheet of plastic;

5 an underlayer coating, on the sheet of plastic, comprising a first polymer material comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed.

10 2. A substrate according to claim 1 wherein the overlayer is substantially free of particulate matter.

15 3. A substrate according to claim 1 or claim 2 wherein the overlayer is substantially wax and pigment free.

4. A substrate suitable for printing a toner image thereon, comprising:
a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

20 an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer, characterized in that the overlayer is substantially wax and pigment free.

25 5. A substrate according to claim 4 wherein the overlayer is substantially free of particulate mater.

30 6. A substrate suitable for printing a toner image thereon, comprising:
a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer,

5 characterized in that the overlayer is substantially free of particulate matter.

7. A substrate according to any of the preceding claims wherein the sheet of plastic is polyethylene.

10 8. A substrate according to any of claims 1-6 wherein the sheet of plastic is vinyl.

9. A substrate according to any of claims 1-6 wherein the sheet of plastic is polycarbonate.

15 10. A substrate according to any of claims 1-6 wherein the sheet of plastic is PET.

11. A substrate according to any of claims 1-6, wherein the sheet of plastic is BOPP.

20 12. A substrate according to any of the preceding claims wherein the overlayer comprises styrene butadiene copolymer.

13. A substrate suitable for printing a toner image thereon, comprising:

a sheet of BOPP plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material;

25 an overlayer coating, directly on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be fused and fixed, the second polymer consisting essentially of a polymer chosen from the group consisting of ethylene acrylic acid copolymer and polyvinyl pyridine.

30 14. A substrate according to any of claims 1-11 or 13, wherein the overlayer comprises ethylene acrylic acid copolymer.

15. A substrate according to claim 14 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

16. A substrate according to claim 14 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 16%.

17. A substrate according to any of claims 14-15 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.

18. A substrate according to any of claims 14-15 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.

19. A substrate according to any of claims 1-11 or 13 wherein the overlayer comprises polyvinyl pyridine.

20. A substrate according to any of the preceding claims wherein the underlayer comprises amine terminated polyamide.

21. A substrate according to any of claims 1-19 wherein the underlayer comprises a silane coupling agent.

22. A substrate according to any of claims 1-19 wherein the underlayer comprises amino propyl triethoxy silane.

23. A substrate according to any of the preceding claims wherein the underlayer has a weight of between 0.1 and 1 grams per square meter.

24. A substrate according to any of the preceding claims wherein the underlayer has a weight of between about 0.3 and 0.5 grams per square meter.

25. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.1 and 10 grams per square meter.

26. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.2 and 2 grams per square meter.

27. A substrate according to claim 26 wherein the overlayer has a weight of between about 0.25 and about 0.35 grams per square meter.

28. A substrate according to any of the preceding claims wherein the underlayer is substantially free of particulate matter.

29. A substrate according to any of the preceding claims comprising only two coating layers.

30. A method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer, the underlayer comprising a polymer chosen from the group consisting of amine terminated polyamide, a silane coupling agent and amino propyl triethoxy silane;

directly overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed.

31. A method according to claim 30 wherein the coated substrate is a substrate according to any of claims 1-29.

32. A substrate produced according to the method of claim 30 or claim 31.

33. A substrate comprising a sheet of BOPP and an outer coating consisting substantially only of a polymer chosen from the group consisting of ethylene acrylic acid copolymer, and polyvinyl pyridine.

34. A substrate according to claim 33 wherein the coating comprises polyvinyl pyridine.

35. A substrate according to claim 33 wherein the coating comprises ethylene acrylic acid copolymer.

36. A substrate according to claim 35 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

37. A printing method comprising:

providing a substrate according to any of claims 1-29 or 32-36 or produced according to claim 30 or claim 31; and

printing a toner image on the substrate.

38. A printing method according to claim 37 wherein the toner image is a liquid toner image.

39. A printing method according to claim 37 or claim 38 wherein printing comprises transferring the toner image to the substrate using heat and pressure.

40. A printing method according to claim 37 or 38 wherein printing comprises electrostatically transferring the toner image to the substrate.

41. A printing method according to any of claims 37-40 and comprising:

forming the image on an image forming surface;

transferring the image from the image forming surface to an intermediate transfer member; and

transferring the image from the intermediate transfer member to the substrate.

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Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

COATING SYSTEM FOR SUBSTRATES

the specification of which

(check one)

- ☐ is attached hereto.
- ☒ was filed on October 8, 1998 as United States Application No. or PCT International Application Number PCT/IL98/00491 and was amended on November 12, 1999

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>121951</u>	<u>Israel</u>	<u>12 October 1997</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u>PCT/IL97/00391</u>	<u>PCT - RO/IL</u>	<u>27 November 1997</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u></u>	<u></u>	<u></u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

_____	_____
(Application Serial No.)	(Filing Date)
_____	_____
(Application Serial No.)	(Filing Date)
_____	_____
(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

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